

PHYS393 lecture summaries

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1 Basic Statistical Mechanics

This introduces the basic ideas using a system of distinguishable particles, e.g. magnetic ions in a paramagnetic salt. The initial goal is to find the heat capacity C . We can get this if we know the total energy U .

Each particle has energy levels $\varepsilon_1, \varepsilon_2, \dots$ with n_1, n_2, \dots particles respectively.

In real systems, there may be constraints like total particle number N and energy U must be fixed.

For given constraints, we assume that the particles are equally likely to have any arrangement (or microstate) among the energy levels.

We want to find

$$U = n_1\varepsilon_1 + n_2\varepsilon_2 + \dots,$$

so we need to know the most likely energy distribution (n_1, n_2, \dots) (or macrostate).

"Most likely" means that number of arrangement

$$\Omega = \frac{N!}{n_1!n_2!\dots}$$

is largest. We need to find the unknown (n_1, n_2, \dots) when Ω is maximum.

This is tricky when we have constraints on N and U . We need to use the Lagrange multiplier method. Instead of Ω , we find the maximum of

$$L = \ln \Omega + \lambda_1 N + \lambda_2 U$$

where λ_1, λ_2 are additional unknowns.

Using Stirling's approximation,

$$\ln n! \approx n \ln n - n$$

we then differentiate L with respect to n_i and solve for n_i . For just this differentiation, we assume that terms N and U in L are not fixed and are functions of n_i (but N in the Ω function is still fixed).

Together with the Boltzmann postulate

$$S = k_B \ln \Omega$$

and the entropy relation

$$dS = \frac{dQ}{T}.$$

the final solution is Boltzmann distribution

$$n_i = A \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$$

An important implication is that at the microscopic level, temperature can be determined by particle populations (n_1, n_2, \dots) - e.g. negative temperature (e.g. laser), magnetic cooling.

To get U , we also need ε_i . E.g. in a spin-1/2 salt, these are $-\mu_B B$ and $+\mu_B B$. Substituting these into Boltzmann distribution and solving for A gives

$$U = -N\mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right)$$

2 Ideal Gas

In an ideal gas, we assume that the particles do not interact with each other. Because of the large number of energy levels ε_i , it may be convenient if the sum for U can be approximated to an integral. So we need a way to find the number of states in $d\varepsilon$.

We solve Schrödinger's equation for a particle in a cubic box of side a . The solution can have the form

$$\psi = A \sin k_x x \sin k_y y \sin k_z z$$

We need only positive k_x, k_y, k_z because the negative values only changes the sign of the wavefunction and gives the same state. The other parts of the solution are

$$\varepsilon = \frac{\hbar^2 k^2}{2m} \text{ and } k^2 = k_x^2 + k_y^2 + k_z^2$$

Assuming that potential is infinity at the walls, wavefunction goes to zero there. This results in the quantisation conditions

$$k_x = \frac{n_x \pi}{a}, k_y = \frac{n_y \pi}{a} \text{ and } k_z = \frac{n_z \pi}{a}$$

The possible points in k space give a 3D grid of points π/a apart. If we divide the space into identical cubes centered at every point, we can associate the volume $(\pi/a)^3$ with each point.

By considering the volume of a spherical shell of radius k and thickness dk , we can count the number of states in the shell:

$$g(k)dk = 4\pi k^2 dk \div (\pi/a)^3 \div 8$$

This defines $g(k)$, the density of states. k is related to ε . In the corresponding $d\varepsilon$, there are the same number of states:

$$g(\varepsilon)d\varepsilon = g(k)dk$$

This gives the density of states in energy variable

$$g(\varepsilon) = \frac{4\pi m V}{h^3} \sqrt{2m\varepsilon}$$

If we know the number of particles $f(\varepsilon)$ in a state, the total energy is

$$U = \int_0^\infty \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon$$

$f(\varepsilon)$ corresponds to n_i . We can find it using the Lagrange multiplier method again. This time, the particles are indistinguishable.

We consider arrangements of particles and states in $d\varepsilon$, obtain an expression for all energy and maximise this with constraints on N and U . For a typical gas at room temperature, the number of particles in any $d\varepsilon$ is much smaller than the number of states. This assumption leads to the Boltzmann distribution again:

$$f(\varepsilon) = A \exp\left(-\frac{\varepsilon}{k_B T}\right)$$

The integral above can now be solved to give

$$U = \frac{3}{2}N_A k_B T$$

for 1 mol of the gas and heat capacity

$$C = \frac{3}{2}N_A k_B.$$

3 Electrons in Metals

A simple model of electrons in metals assumes that the conduction electrons form a gas. It neglects the rest of the atoms. This model looks like an ideal gas, but the measured electronic heat capacity of a metal is much smaller.

The difference is because of Pauli's exclusion principle. At room temperature, electrons in metals stack up in energy levels. There is not free states above for them to get excited to - unless they are very near the top - the Fermi level.

To find C , we can follow similar steps to ideal gas. The density of states is doubled because there are 2 spin states for each energy state:

$$g(\varepsilon) = 2 \times \frac{4\pi m V}{h^3} \sqrt{2m\varepsilon}$$

We find the number of arrangements of particles among states in each interval $d\varepsilon$ following similar steps as ideal gas. But we do not assume that the number of particles in any $d\varepsilon$ is much smaller than the number of states. We must also insist that no 2 particles can be in the same state.

Then applying the Lagrange multiplier method with the constraints on N and U gives the Fermi-Dirac distribution:

$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon - \mu)/k_B T] + 1}$$

where μ is an unknown constant that depends on N and T . At $T = 0$, $f(\varepsilon)$ is 1 when ε is below μ and 0 otherwise. Then number of states below μ must equal number of particles. The relation can be written as

$$\int_0^\mu g(\varepsilon) d\varepsilon = N$$

Then we can solve for μ . Its value at 0 K is called Fermi energy:

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

To find the heat capacity, we estimate the number n of electrons excited above E_F . Obtain the approximate distribution above E_F

$$f(\varepsilon) = e^{\mu/k_B T} e^{-\varepsilon/k_B T}$$

The width of $k_B T$ means that

$$n \approx g(E_F) k_B T$$

Since this $f(\varepsilon)$ has the same form as Boltzmann distribution, the ideal gas result applies. So total energy of excited electrons is

$$U_1 = n \times \frac{3}{2} k_B T$$

Combining these results gives the molar heat capacity as

$$C = \frac{dU}{dT} = \frac{9}{2} \frac{k_B T}{E_F} R$$

4 Phonons and Photons

4.1 Phonons

Heat capacity of a solid also comes from vibration of atoms. This can be modelled as sinusoidal waves of displacements of atoms from rest positions.

If we assume that these displacements are zero at the sides of a solid cube, we get the same quantisation conditions as ideal gas. This mean we can use the same density of states. But we must multiply that by 3 because for each wavevector (k_x, k_y, k_z) , there can be 2 transverse and 1 longitudinal polarisations.

Another difference is that angular frequency ω is often used instead of ε . The relation with wavevector is

$$\omega = vk$$

where v is speed of sound in the solid. Transform density of states formula using

$$g(\omega)d\omega = g(k)dk$$

to get

$$g(\omega) = 3 \times \frac{V\omega^2}{2\pi^2v^3}$$

Waves with frequency ω are quantised into packets of energy

$$\varepsilon = \hbar\omega$$

Think of packets as particles - called phonons. Obtain their energy distribution $f(\varepsilon)$ using similar steps as for electron gas but without exclusion principle. Also no constraint on particle number because phonons are virtual particles. Lagrange multiplier method then gives

$$f(\omega) = \frac{1}{\exp(\hbar\omega/k_B T) - 1}$$

No μ because no constraint on N . Integrate $\hbar\omega f(\omega)g(\omega)$ to find U . But upper limit is not infinity - because cannot have wavelength smaller than spacing between atoms. Expression for total energy is

$$U = \int_0^{\omega_D} \hbar\omega f(\omega)g(\omega)d\omega$$

for some maximum ω_D called Debye frequency. To obtain this, use maths result that number of possible modes for N atoms is $3N$. (A mode is a wave with a particular polarisation and wavevector.) Then

$$3N = \int_0^{\omega_D} g(\omega)d\omega$$

Solving gives

$$\omega_D = \left(\frac{6N\pi^2v^3}{V} \right)^{1/3}$$

Combining the above gives

$$U = \frac{3V\hbar}{2\pi^2v^3} \int_0^{\omega_D} \frac{\omega^3 d\omega}{\exp(\hbar\omega/k_B T) - 1}$$

At the high and low temperature limits, this can be solved. The resulting heat capacities are respectively

$$C = 3Nk_B \text{ and } C = AT^3$$

where A is an expression containing the constant factors in the above integral.

4.2 Photons

A hole on a hollow box acts like black body in absorbing all radiation falling on it. The energy interacts with the inner walls, achieve thermal equilibrium and gets remitted through the hole. This is blackbody radiation. Instead of heat capacity, we are interested here in its frequency spectrum.

The steps are very similar to phonons. Instead of atomic vibration, we have electromagnetic waves here. Assuming a perfectly conducting box, electric field parallel to inner walls must be zero. Assuming sinusoidal waves, this boundary condition gives the same quantisation conditions as ideal gas.

This should mean the same density of states (DOS). But because the wave of each wavevector can have 2 transverse polarisation, the ideal gas DOS must be multiplied by 2. Like phonons, we work in variable ω . Transforming to this gives

$$g(\omega) = 2 \times \frac{V\omega^2}{2\pi^2c^3}$$

where v is now speed of light c . Wave packet energy and $f(\omega)$ are the same as phonons. But instead of finding the total U , we want the frequency distribution of energy $u(\omega)$. This the energy per unit frequency:

$$u(\omega) = \hbar\omega f(\omega)g(\omega) = \frac{V\hbar\omega^3}{\pi^2c^3} \frac{1}{\exp(\hbar\omega/k_BT) - 1}$$

which is the blackbody radiation spectrum.

5 Dilution Cooling

Liquid helium is used for cooling by evaporating it. Lowest temperature is limited to about 1 K - its vapour pressure falls exponentially and it cannot evaporate much below 1 K.

A mixture of helium-3/helium-4 can cool down to mK. Below about 1 K, the mixture separates into 2 layers. The phase more concentrated in helium-3 about the phase more dilute. Cooling happens when helium-3 diffuses from upper to lower layer.

This downward movement corresponds to the upward movement of vapour when liquid helium evaporates. The concentration of helium-3 in lower layer corresponds to vapour pressure of liquid helium. Below a few mK, the saturation concentration of lower layer remains fixed at 6.6%. So helium-3 can

continue to diffused downwards as long as the lower layer is not saturated. This is the advantage over evaporating liquid helium whose vapour pressure quickly goes to zero below 1 K.

Two ways to explain why cooling takes place:

1. Increase in entropy in lower layer.

First, obtain the heat capacity for each layer. Helium-3 atoms are fermions like electrons. Use the formula from electron gas for molar heat capacity:

$$C = \frac{\pi^2}{2} \frac{T}{T_F} R$$

where Fermi temperature T_F is E_F/k_B . Compute heat capacities for each layer using correct effective mass ratios and molar volumes..

Integrate $dS = dQ/T$ to find entropy. Use 3rd law of thermodynamics to set the lower limit, and use the C formula to integrate. Result is

$$S = C$$

This shows that molar entropy S_D of lower layer is higher than that of upper layer S_C . So when helium-3 flows to lower layer, increase in entropy requires heat absorbed from surrounding - which then cools down.

Combining the above, heat change when 1 mol of helium-3 flows to lower layer is

$$\Delta H = T(S_D - S_C) = 84T^2 \text{ J/K}$$

2. Increase in excited particles.

Since helium-3 are fermions, we can use the expression for number of excited electrons

$$n \approx g(E_F)k_B T = \frac{3N}{2E_F} k_B T$$

Lower layer has lower E_F because of lower concentration N/V . So it has more excited helium-3.

Average energy of excited helium-3 is the same $3k_B T/2$ in both layers. So total energy of excited helium-3 is higher in lower layer. In moving to lower layer, helium-3 must gain energy. It has to absorb this from the surrounding - which then cools down.

6 Magnetic Cooling

This method can cool down to microKelvin. Consider a paramagnetic salt first. The possible steps are: 1. Start at liquid helium temperature; 2. Magnetise isothermally; 3. Demagnetise adiabatically.

Step 2: Consider a spin-1/2 salt. Increasing applied field increases spacing between magnetic energy levels. As higher level moves up, particles fall to lower level to obey Boltzmann distribution. So heat is given out. Magnetising it slowly gives the heat time to dissipate so temperature stays the same.

Step 3: Then thermally isolate the salt. When field decreases, energy spacing decreases. As higher level moves down, particles should move back up from lower level. But they cannot - because they cannot get energy to do this since the salt is thermally isolated. According to

$$n_2 = A \exp\left(-\frac{\mu_B B}{k_B T}\right)$$

if n_2 is fixed, then B/T is fixed. So as field decreases, temperature must fall.

If B falls to zero, T cannot go to zero because of field from neighbouring magnetic ions. This field determines the Curie temperature T_c below which the ions align themselves and become ferromagnetic. Then the salt stops working because it cannot respond to the external field. So T_c gives a lower limit for the cooling.

For paramagnetic salt, T_c is in the milliKelvins. So it is not possible to reach microKelvin using this salt. Another material whose ions give much smaller field is needed. The nucleus would do. The nuclear magneton is about 2000 times smaller than the Bohr magneton for electron. So the field would be 2000 times smaller also. Then T_c would be well below microKelvin. Typically, a block of copper is used in nuclear cooling.

In practice, it takes a long time - days, weeks - to reach the the final temperature. To speed things up:

1. Nuclear cooling starts at milliKelvin, e.g. using a dilution refrigeration.
2. It uses much more power magnet. The small μ_n also mean small energy spacing. Stronger field to increase this spacing would reduce the particles at the higher level. When demagnetised, fewer particles at higher level means lower temperature (for the same final field).

7 Superfluid

8 Superconductor